Contract Report

High Throughput, Low Toxic Processing of Very Thin, High Efficiency CIGSS Solar Cells

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1: INTRODUCTION

The major concern in the photovoltaic industry is to find a way to reduce the cost below $1.00/peak watt to make the technology economically viable. Keeping this goal in mind the research activities are focused on developing highly efficient thin-film solar cells capable of being produced using an economical process. $CuIn_{1-x}Ga_xSe_{2-y}S_y$ (CIGSeS) and $CuIn_{1-x}Ga_xS_2$ (CIGS2) are potential candidates for this purpose. Efficiency of 19.5% [1] has been achieved on $CuIn_{1-x}Ga_xSe_2$ (CIGS) deposited using co-evaporation. Sputtering is the technique capable of providing high yield and higher production rates. Research activities presented here focus on developing CIGSeS thin films by depositing elemental precursor Cu-In-Ga by sputtering technique followed by selenization/sulfurization in either conventional furnace or by rapid thermal processing. So far, experiments were carried out to optimize conditions for both conventional and rapid thermal processing approaches. Also experiments were conducted on very thin absorber layers with both the conventional and rapid thermal processing approaches. These initial experiments towards optimizing the selenization parameters were discussed in detail in earlier reports. There is a drive towards thinner CIGS2 films to reduce the consumption of indium and gallium due to increasing costs of these elements. Efforts are being made to reduce the thickness while maintaining high efficiency. Experiments were carried out for this purpose. The thickness of the absorber was reduced systematically from 2.7 μm to 2 μm and further to 1.2 μm and characterization was carried out.

During this quarter, experiments were carried out to optimize the metallic precursor deposition for standard absorber preparation and selenization/sulfurization parameters for the conventional furnace and rapid thermal processing. Efforts were also taken to reduce the absorber thickness systematically and understand the issues involved with the thickness reduction. Experiments were carried out to study the effects of Na content on the surface morphology and the grain structure of the absorber film. Also maintenance of mechanical pump used for initial vacuum of the sputtering chambers was completed. The substrate moving mechanism in the sputtering chambers was repaired and few changes were made to the mounting fixture of this assembly for better operation and to avoid future damage.

2: OPTIMIZATION OF METALLIC PRECURSOR DEPOSITION FOR CIGSeS AND SELENIZATION/SULFURIZATION IN THE CONVENTIONAL FURNACE

Earlier, PV Mat Lab at the Florida Solar Energy Center achieved the world record efficiency of 13.73% on CIGSeS thin film solar cell on small area by the sputtering-conventional furnace. After achieving the highest efficiency experiments were carried out to improve the material quality to further increase the efficiency. A detailed study is being carried out by varying the process parameters.

Experimentation:

For this set of experiments, CIGSeS thicknesses in the range of 2-2.3 μm were chosen. The sputtering rates for CuGa and In calibrated earlier with the respective sputtering powers and argon pressures were maintained. CuGa content was kept constant by keeping the substrate movement speed constant for all CuGa depositions. Cu/(In+Ga) ratio was systematically increased by reducing the indium content, i.e. by increasing the substrate movement speeds over the indium target while keeping the deposition rate constant. Three different indium contents 1. high, 2. intermediate (9% less) and 3. low (16% less) corresponding to low, intermediate, and high substrate movement speeds were chosen.

Presence of small amount of sodium during CIGS formation has proven to be beneficial. Substrates for the CIGSeS thin film fabrication were chosen with and without the alkali barrier. Sodium containing precursor, NaF film was deposited prior to the precursor deposition on the molybdenum coated substrate with an alkali barrier. CIGSeS absorbers were fabricated on soda lime glass (SLG) substrates with an alkali barrier and NaF thicknesses of 80 Å and 120 Å. Absorbers were also prepared on SLG with no barrier with no NaF and 40 Å of NaF.

The CIGSeS thin film absorbers were prepared in the two stage process. Stage one consisted of the deposition of CuGa-In metallic precursors on molybdenum coated SLG substrates. Stage two consisted of the selenization and sulfurization of the metallic precursors in the diethyl selenium (DESe) and H_2S ambient respectively. Selenization and sulfurization of the entire elemental stack was carried out at 500 ºC and 515 ºC.

Chemical composition of the film was studied by electron probe microanalysis (EPMA) at NREL and X-ray energy dispersive spectroscopy (XEDS) analysis at MCF/UCF. Crystalline structure and morphology of the films was analyzed by atomic force microscopy (AFM) at NREL.

Results and Discussion:

Composition

The atomic concentrations of elements Cu, In, Ga, Se and S and Cu/In+Ga ratios for CIGSeS thin film with 1. high, 2. intermediate (9% less) and 3. low (16% less) indium contents corresponding to low, intermediate and high substrate movement speeds over the indium targets are shown in the Tables 1, 2 and 3 respectively. The compositions analyzed by EPMA using electron beam energies of 10 kV and 20 kV correspond respectively to the near the surface of the film and bulk of the film. Letters U and E at the end of the sample identification number correspond to unetched and etched absorber films respectively. As can be seen from Table I, Cu/In+Ga ratios for the high indium content are in the range 0.76 – 0.83 for the unetched samples. Cu/(In+Ga) ratios for CIGSeS thin films with intermediate and low indium depositions tend to exceed 1 indicating their overall Cu-rich nature for the unetched samples (Table II and Table III).

Experiments were also carried out to optimize the selenization and sulfurization timings. Table I shows that S/(Se+S) ratios are 0.032–0.062. In the subsequent experiments, selenization time was reduced while increasing the sulfurization time. Consequently significantly higher S/(Se+S) ratios in the range 0.213-0.287 were obtained (Tables II and III). Experiments are being carried out to further optimize (reduce) the S/(Se+S) ratio.

Table I: Chemical composition of unetched and etched CIGSeS absorbers with 80 and 120 Å NaF layer and high indium content as analyzed by EPMA at 10 kV and 20 kV e-beam energy

ID	NaF	Voltage	Cu	In	Ga	Se	S	Cu/(In+Ga)	S/(Se+S)
VK1U	120 Å	10 kV	23.07	26.67	1.02	46.37	2.88	0.833	0.058
VK1U	120 Å	20 kV	22.13	24.86	3.38	47.45	2.18	0.784	0.044
VK3U	80 Å	10 kV	22.37	27.00	1.32	47.24	2.08	0.790	0.042
VK3U	80 Å	20 kV	22.05	25.53	3.08	47.76	1.58	0.771	0.032
VK2E	120 Å	10 kV	22.77	26.98	1.02	46.17	3.06	0.813	0.062
VK2E	120 Å	20 kV	21.87	25.25	3.36	47.12	2.40	0.764	0.049
VK4E	80 Å	10 kV	22.10	27.32	1.37	46.89	2.32	0.770	0.047
VK4E	80 Å	20 kV	21.86	25.66	3.13	47.57	1.77	0.759	0.036

Table II: Chemical composition of unetched and etched CIGSeS absorbers with No NaF layer and intermediate indium content as analyzed by EPMA at 10 kV and 20 kV e-beam energy

ID	NaF	Voltage	Cu	In	Ga	Se	S	Cu/(In+Ga)	S/(Se+S)
N3bU	No	10 kV	25.78	22.16	3.51	34.66	13.89	1.004	0.286
N3bU	No	20 kV	25.33	20.32	5.13	36.53	12.70	0.996	0.258
N3bE	No	10 kV	24.01	23.61	3.80	34.62	13.95	0.876	0.287
N3bE	No	20 kV	23.79	21.05	5.41	37.14	12.59	0.899	0.253

Table III: Chemical composition of unetched and etched CIGSeS absorbers with 40 Å NaF layer and low indium content as analyzed by EPMA at 10 kV and 20 kV e-beam energy

ID	NaF	Voltage	Cu	In	Ga	Se	S	Cu/(In+Ga)	S/(Se+S)
N4bU	40 Å	10 kV	26.51	21.93	3.01	34.60	13.95	1.063	0.287
N4bU	40 Å	20 kV	25.96	20.54	4.85	37.69	10.96	1.022	0.225
N4bE	40 Å	10 kV	24.40	23.69	3.03	35.79	13.10	0.913	0.268
N4bE	40 Å	20 kV	23.79	22.02	4.76	38.91	10.52	0.888	0.213

X-ray energy dispersive spectroscopy was also carried out as a routine analysis while awaiting the EPMA results. (Fig. 1).

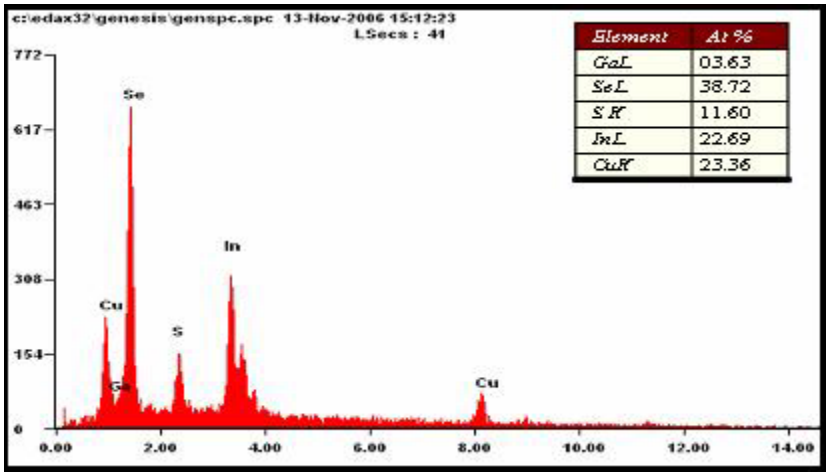


Fig. 1: XEDS Analysis of CIGSeS Thin Film

Morphology:

Fig 2 and Fig 3 show the 2D and 3D AFM micrographs respectively of the CIGSeS thin film selenized/sulfurized at 515 °C for 50/11 minutes. This film was fabricated on SLG with an alkali barrier with 120 Å NaF and high indium content. Fig. 2 and Fig. 3 show that the film has compact morphology and grain distribution. The average roughness, Ra of the film was 142 nm. 3D micrograph reveals the formation of islands and the grains. Fig 3 reveals the formation of facets. The formation of facets is attributed to the higher selenization and sulfurization temperature.

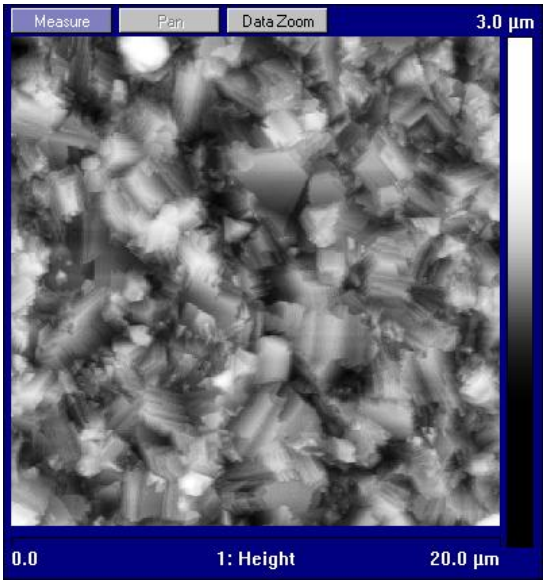


Fig. 2: AFM 2D micrograph of CIGSeS thin film with high indium content and 120 Å NaF, selenized (50 min) and sulfurized (11 min) at 515 °C

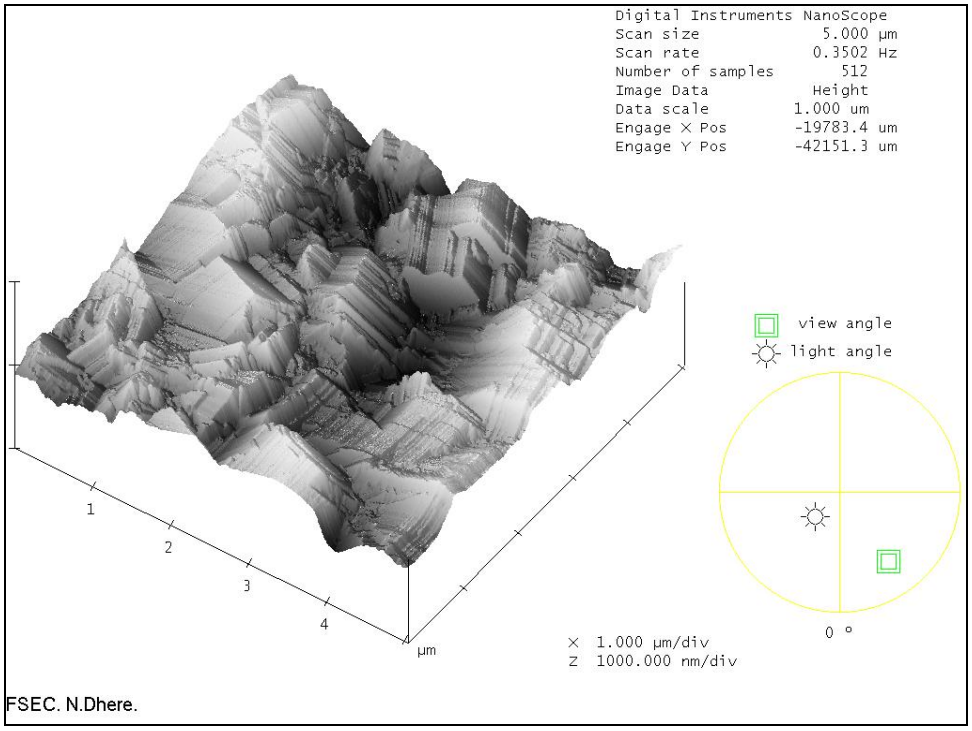


Fig. 3: AFM 3D micrograph of CIGSeS thin film with high indium content and 120 Å NaF, selenized (50 min) and sulfurized (11 min) at 515 °C

3: RAPID THERMAL PROCESSING

Further optimization of the RTP process is being carried out after obtaining encouraging efficiencies (12.78%) [2]. Currently experiments are done to optimize the Cu/In+Ga ratio and the sodium content. These CIGSeS films do have high indium content. During CuGa and indium sputtering, substrate movement speed was kept at 50 seconds/1" and 82.5 seconds/1" respectively. Detailed material and photovoltaic characterization is being carried out by EPMA, XEDS, XRD, optical microscopy, SEM, AFM, TEM, I-V and QE techniques.

Composition:

The EPMA results of the CIGSeS samples are given in following table IV. Letters U and E at the end of the sample identification number correspond to unetched and etched absorber films respectively. The Cu/In+Ga ratio (for unetched samples) near the surface is ~ 0.84 to 0.92 and in the bulk for unetched samples is ~0.82 to 0.84.

Table IV: EPMA analysis for CIGSeS sample fabricated by RTP.

Sample ID	NaF (Å)	Voltage (kV)	Cu	In	Ga	Se	S	Cu/In+Ga	S/Se+S
SK16U	120	10	23.37	26.20	1.49	27.80	21.14	0.84	0.43
SK16U	120	20	22.73	24.24	3.61	30.84	18.57	0.82	0.38
SK17U	80	10	24.62	25.49	1.17	34.98	13.73	0.92	0.28
SK17U	80	20	23.04	24.00	3.53	36.47	12.97	0.84	0.26
SK16E	120	10	23.19	26.75	1.20	25.86	23.01	0.83	0.47
SK16E	120	20	22.14	24.56	3.82	28.37	21.11	0.78	0.42
SK17E	80	10	23.39	26.31	1.26	29.49	19.56	0.85	0.40
SK17E	80	20	22.89	24.39	3.44	31.32	17.96	0.82	0.36

Morphology:

Following images show AFM analysis of CIGSeS samples fabricated by RTP.

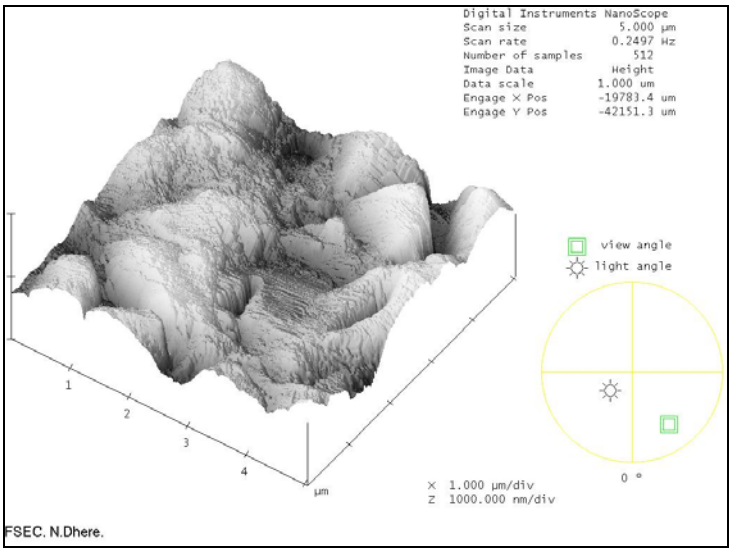


Fig.4: AFM 3D surface topography of CIGSeS thin film (Sample SK16E)

AFM three dimensional CIGSeS sample surface topography is shown in Fig. 4. Grain size of ~1 to 2 microns can be seen. RTP films usually have comparatively smaller grains as the time for film formation is low.

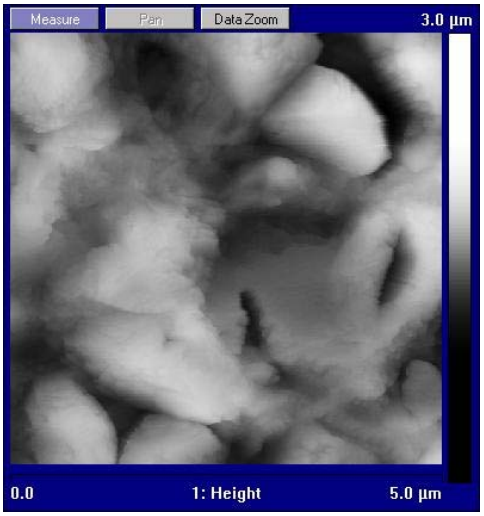


Fig. 5: AFM 2D image of CIGSeS thin film (Sample SK16E)

AFM surface image of the surface of CIGSeS sample fabricated by RTP is shown in Fig.5 Morphology of the grains is evident from the AFM surface image. The film is compact with hillocks and valleys.

Further experimentation and characterization is being carried out.

4: THICKNESS REDUCTION OF ABSORBER LAYER IN CIGS2 THIN FILM SOLAR CELLS

CIGS2 thin films were prepared in two stages. Stage one consisted of the deposition of CuGa-In metallic precursors with Cu/(In+Ga) ratio of 1.4 on molybdenum coated glass substrates. During CuGa and indium sputtering, substrate movement speed was kept at 84 seconds/1" and 78 seconds/1" respectively. This produced an absorber of thickness 2.7 μm. To produce absorbers of thicknesses 2 μm and 1.2 μm, the substrate movement speeds were reduced proportionately. Stage two consisted of the sulfurization of these metallic precursors in dilute H_2S (4-8% H_2S) ambient. The copper rich $Cu_{2-x}S$ layer that segregated on the surface of near stoichiometric, copper-poor CIGS2 thin film was etched away in a 10% KCN solution.

Composition:

The EPMA results for Cu/ (In+Ga) ratio are given in Table V. The compositions analyzed by EPMA using electron beam energies of 10 kV and 20 kV correspond respectively to the near the surface of the film and bulk of the film. For the entire sample IDs, suffix S indicates sulfurized and etched absorber. Prefix 16 indicates an absorber of thickness 2.7 μm, while prefix 15 and prefix 18 indicate absorbers of thicknesses 2.0 μm and 1.2 μm respectively. Cu/ (In+Ga) is in the near stoichiometric range of 0.85-1.0 for all the etched absorber samples.

Table V: EPMA results for CIGS2 etched absorbers.

Sample ID	Voltage (kV)	Cu	In	Ga	S	Cu/In+Ga
15 S	10	23.56	25.63	2.47	48.31	0.84
15 S	20	23.95	20.93	5.15	49.95	0.91
16 S	10	23.88	24.87	2.94	48.28	0.86
16 S	20	23.96	21.03	5.41	49.58	0.94
18 S	10	24.90	20.12	6.16	48.80	0.94
18 S	20	25.84	15.49	8.86	49.79	1.06

Crystallographic structure:

Figures 6, 7 and 8 show the XRD patterns for etched absorbers of thicknesses 2.7 μm, 2.0 μm and 1.2 μm respectively. Comparing the XRD patterns, it is seen that as the thickness reduces to 2.0 μm and further to 1.2 μm, intensity of all the peaks is reduced. It can be deduced that the chalcopyrite CIGS2 phase is formed.

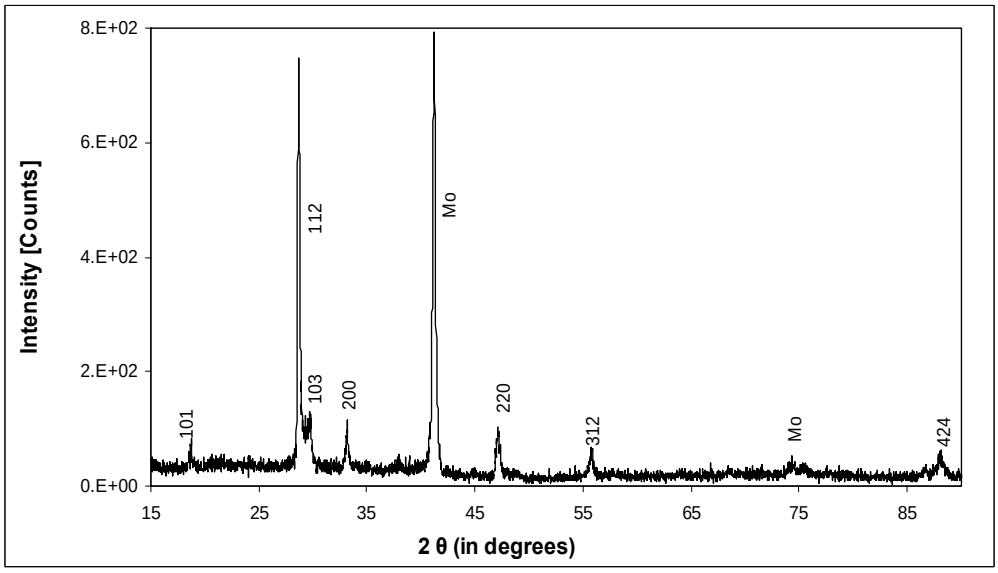


Fig 6. XRD pattern for 2.7 μm thick CIGS2 absorber

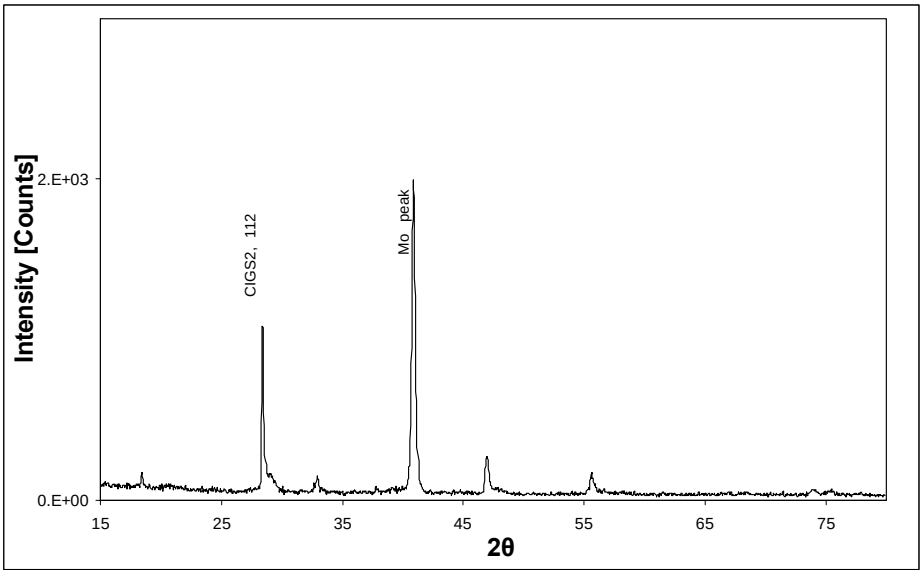


Fig. 7: XRD pattern for 2.0 μm thick CIGS2 absorber

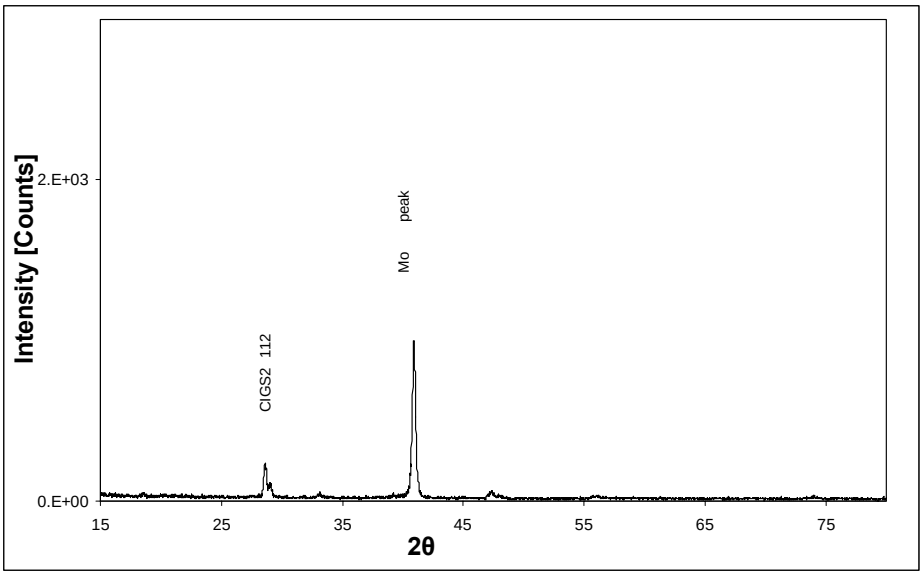
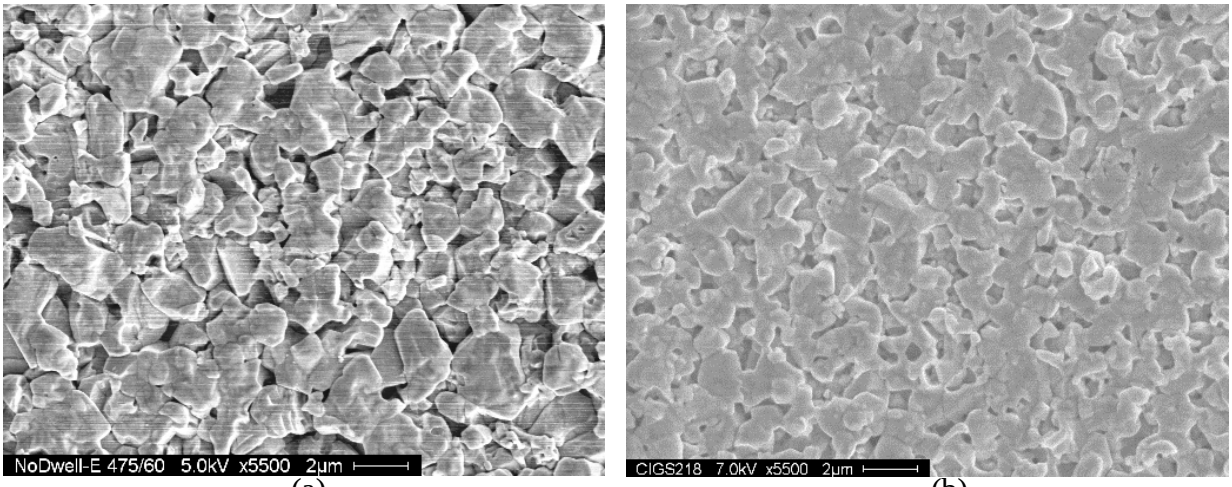


Fig. 8: XRD pattern for 1.2 μm thick CIGS2 absorber

Morphology:

Scanning Electron Microscopy:

Figure 9 shows the SEM images of the 2.7 μm and 1.2 μm thick absorber layer from these images we can see clearly that the thicker film has better faceted grain structure as compared to the thin absorber layer. Average grain size found by intercept method is 1.4 μm for an absorber of thickness 2.7 μm (Fig. 9a) and 1.2 μm for an absorber of thickness 1.2μm (Fig. 9b).

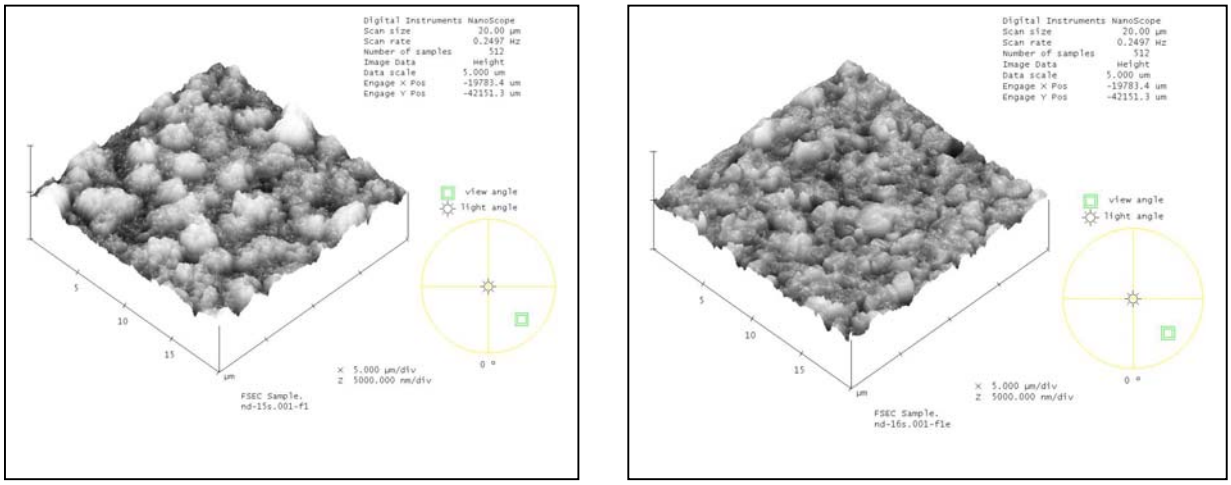


(a) (b)

Fig 9. SEM images (a) 2.7 μm (b) 1.2 μm CIGS2 etched absorber

Atomic Force Microscopy:

Figure 10a and 10b shows the AFM images for absorbers with thicknesses 2.7 μm and 1.2 μm respectively. It is visible that absorber in both cases is compact and continuous, with some hillocks and valleys. The hillocks and valleys form due to the difference the coefficients of thermal expansion between substrate and material.



(a) (b)

Fig. 10: AFM images (a) 2.7 μm (b) 1.2 μm

Current-Voltage Characterization:

These absorber layers were processed and solar cells were completed by deposition of CdS by CBD technique followed by the window layer deposited by RF magnetron sputtering. Current-voltage measurements were carried out on these solar cells at FSEC. The photovoltaic parameters are summarized in the Table VI. After the preparation of 2.7 μm absorber, the deposition system was under maintenance for some time. Moreover, it has been found recently that the sulfurization set-up needs servicing. These seem to have affected the 2 μm and 1.2 μm CIGS2 layers and cells. It is expected that these results would improve after tune up of the systems.

Table VI: Comparison of Photovoltaic Parameters

Absorber	**Efficiency (%)**	**Fill factor**	**V_{oc} (mV)**	**I_{sc}(mA)**
2.7 µm	10.0	63.07	810	8.6
2.0 µm	5.55	53.51	720	6.3
1.2 µm	3.93	51.51	640	5.3

5: MAINTENANCE

5.1 Mechanical Pump Maintenance

The CIGSeS thin films are prepared by depositing CuGa-In metallic precursors on molybdenum coated glass substrates by using DC magnetron sputtering, after selenization/sulfurization and CdS hetrojunction partner layer deposition on CIGSeS layer, the next step is to carry out ZnO/ZnO:Al window bilayer deposition by RF magnetron sputtering. The systems are pumped by combinations of cryopumps and mechanical vacuum pumps. After the maintenance of the cryopumps it was also observed that the pump down rate of the mechanical pump had deteriorated and maintenance of the mechanical pump was required.

The maintenance kit and krytox oil for this mechanical pump were procured for this reason. Once the maintenance of the pump was carried out the initial pumping down of the sputtering chambers was back to normal. With the completion of maintenance of the mechanical pump, sputtering of CuGa and In metallic precursors and i-ZnO/ZnO:Al window bilayer are being carried out routinely.

5.2 Substrate Moving Mechanism

During the sputtering of the metallic precursors and the window layer the substrate is moved at constant speed over the sputter targets to obtain uniform thickness of the film. Due to heavy use and general wear and tear the connector feed-through connecting the stepper motor to the rotating shaft in the system for deposition of the i-ZnO/ZnO:Al window bilayer was damaged. A new feed-through was procured. It was also observed that the rotating shaft and the stepper motor fixture were misaligned. They were aligned. Similar issues were observed in the case of the system for deposition of molybdenum and CuGa-In metallic precursors. Necessary corrections were made to this fixture too. After fixing up the substrate moving mechanism in both the sputtering chambers, routine depositions were resumed.

6: PRESENTATIONS AND PUBLICATIONS

1. Vinay V. Hadagali and Neelkanth G. Dhere, “Optimization of the Absorber Layer Growth Process for High Efficiency CIGSeS Thin Film Solar Cells” Presentation, AVS 53rd International Symposium and Exhibition, Nov 12 -17, 2006, San Francisco, CA

2. Parag S. Vasekar and Neelkanth G. Dhere, “Morphological changes in CIGS2 upon thickness reduction of absorber layer” Presentation, AVS 53rd International Symposium and Exhibition, Nov 12 -17, 2006, San Francisco, CA

7: REFERENCES

[1] Miguel A. Contreras, K. Ramanathan, J. AbuShama, F. Hasoon, D. L. Young, B. Egaas and R. Noufi, Prog. Photovolt: Res. Appl. 2005; 13:209–216.

[2] High Throughput, Low Toxic Processing of Very Thin, High Efficiency CIGSS Solar Cells, Year 1, Final Report.